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Formation of Amines and Ammonia from Alkyldiazenido Derivatives of Molybdenum and Tungsten

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In previous papers, we [1, 2] and others [3, 4] have reported the reactions of organic halides with coordinated dinitrogen complexes of molybdenum and tungsten to form metal-bound organonitrogen species (*e.g.*, equations 1 and 2; dppe = $Ph_2PCH_2CH_2PPh_2$).

$$Mo(N_2)_2(dppe)_2 + n\text{-}BuBr \rightarrow MoBr(NNBu)(dppe)_2 + N_2 \quad (1)$$

$$W(N_2)_2(dppe)_2 + MeCOCl + HCl \rightarrow WCl_2(N_2HCOMe)(dppe)_2 + N_2 \quad (2)$$

Recently [5], it was reported that treatment of organohydrazido(2–)-complexes of molybdenum and tungsten with lithium aluminum hydride or by base (KOH) distillation gave good yields of secondary amines (*e.g.*, 0.95 mol/mol complex of Me_2NH from $[WBr(N_2Me_2)(dppe)_2]Br$. However, never more than a trace of ammonia was obtained. Hence, one-half of the nitrogen from the original complex was unaccounted for. In this paper, we report the simultaneous formation of a primary amine and ammonia from the reaction of sodium methoxide with alkyldiazenido derivatives of molybdenum and tungsten.

In a typical experiment, sodium borohydride (ten fold excess) in a methanol/benzene solution (rapidly forming sodium methoxide) was added to a benzene solution of $MoBr(NNBu)(dppe)_2$ in an autoclave (1L) under a dinitrogen atmosphere. The sealed system was heated at 100 °C for 10 hr. At the conclusion of the experiment volatiles were removed and trapped (−196 °C) using a vacuum line. The volatiles were treated with 48% hydrobromic acid. The solvents and excess acid were removed *in vacuo* and the residue treated with aqueous sodium hydroxide solution and distilled. Total base was determined (58%) by titration with standard hydrochloric acid. In a separate experiment under identical conditions, the yields of n-butylamine (54%) and ammonia (51%) were determined by gas chromatography using an alkali flame ionization detector [6], and by the indophenol method [7], respectively. The identity of n-butylamine was verified by gas chromatography–mass spectrometry (GC–MS) by comparison with an authentic sample.

Data for the hydrogenation of $MoBr(NNBu)(dppe)_2$ at different temperatures, are given in the Table. Yields are the average of at least two experiments. No change in yield was observed when the reactions were carried out under a dihydrogen rather than a dinitrogen atmosphere. When sodium methoxide was used instead of sodium borohydride, the yield of total base was halved; *e.g.*, 30% at 100 °C for 10 hr. When ethanol/benzene was used instead of methanol/benzene as solvent, the yield of total base was reduced and $MoH_4(dppe)_2$ was formed in about 25% yield based upon available molybdenum. Yield of total base was very low when only methanol was used as solvent. This was probably due to the insolubility of the diazenido complex in methanol.

TABLE. Hydrogenolysis of $MoBr(NNBu)(dppe)_2$.[a]

Temp., °C	Yield (%)	
	n-Butylamine[b]	Ammonia[c]
50	trace	0.5
60	9.6	4.2
65	26.3	26.5
75	32.1	32.6
100	53.8	50.7
125	57.1	48.6
140	55.1	55.6

[a] Reaction carried out in an 1L MagneDrive Autoclave in benzene–methanol solution with *ca.* 10 mol of $NaBH_4$/mol of butyldiazenido complex for 10 hr; N_2 atmosphere. [b] Determined by gas chromatography using an internal standard [6]. [c] Determined by the indophenol method [7].

The gas chromatogram of the aqueous solution after base distillation of the hydrobromide salts revealed a second peak following the n-butylamine peak. This peak was shown to be due to N-butyl-N-methylamine by comparison with an authentic sample using GC–MS. The yield of secondary amine varied from 5 to 20% depending upon the temperature.

It has been demonstrated [8] that methanol alone can reduce coordinated dinitrogen to ammonia under remarkably mild conditions. In the absence of sodium borohydride or sodium methoxide at 85 °C for 84 hr, we have observed no base formation. Similarly, using 5% palladium on charcoal and a dihydrogen atmosphere, we have seen no base formation. Methoxide ion appears to be the reacting species. The presence of N-butyl-N-methylamine may have arisen from a

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reaction of butylamine with formaldehyde, the later arising from hydride transfer from methoxide ion to the metal complex. A large quantity of dppe was recovered from the reaction products but we have not identified any molybdenum-containing products (except when ethanol was used in place of methanol; *vide supra*).

Similar results have been obtained with the cyclohexyldiazenido complex, $MoI(NNC_6H_{11})(dppe)_2$, (ammonia, cyclohexylamine, and N-methylcyclohexylamine) and with $WBr(NNBu)(dppe)_2$. However, in the latter case, at 100 °C for 10 hr, the yield of base was lower (NH_3 = 19%) than for the molybdenum analogue.

Work is in progress to try and elucidate the mechanism of this reaction and identify the molybdenum-containing products.

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